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Note

On the effect of sample factors on the shape of a DTA curve, illustrated by $CuSO_4 \cdot 5H_2O$

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A considerable amount of folk-lore exists as to the effect of such factors as particle-size distribution, packing density and sample dilution on the shapes of DTA curves, but little supporting data are available. The importance of sample variables has long been recognised[1], but the few systematic investigations that have been carried out appear to have been confined to a single substance, or a compound containing impurities. Consequently, the literature offers little guidance as to the choice of an optimum particle-size range for DTA samples, or on the effects which may result from a change in particle-size distribution.

The authors were concerned with the detailed interpretation of DTA curves for certain solid-state decomposition reactions and concluded that it was necessary to obtain more information on the influence of sample factors. Accordingly, a simple and well-characterised system[2-4], involving both decomposition and vaporisation, was chosen for investigation. This was the thermal decomposition of $CuSO_4 \cdot 5H_2O$ in an atmosphere of static air.

The purpose of this note is to draw attention to some of the quite striking changes in the DTA curves brought about solely through variation in sample factors, with other parameters being held constant. Our data show that one, two, or three endothermic peaks can be obtained for the reaction $CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot H_2O$, using a constant heating rate, ambient atmosphere and DTA head assembly. It is therefore hoped that this information will encourage greater caution in the interpretation of single DTA curves, than is sometimes evident in recent scientific publications.

EXPERIMENTAL

The apparatus used was a Standata 6-25 in conjunction with a DTA head assembly type 3474 and platinum sample buckets 8 × 6.2 mm diameter. Static air was used as the sample atmosphere and sintered alumina as the reference material. Except where stated otherwise, a rate of rise in temperature of 10°C min^{-1} was employed.

Analar $CuSO_4 \cdot 5H_2O$ was lightly ground with a mortar and pestle and then hand-sieved through a nest of test sieves (BS Spec. 410/1962) to give seven size fractions, ranging from −14 +18 to −100 +150 mesh. Each fraction was stored in a stoppered container prior to DTA.

RESULTS AND DISCUSSION

Three distinct endothermic processes contribute[2] to the observed endothermic peaks for the decomposition of $CuSO_4 \cdot 5H_2O$ to $CuSO_4 \cdot H_2O$. These are:

$$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot 3H_2O + 2H_2O\ (\text{liquid}) \tag{1}$$

$$H_2O\ (\text{liquid}) \rightarrow H_2O\ (\text{gas}) \tag{2}$$

$$CuSO_4 \cdot 3H_2O \rightarrow CuSO_4 \cdot H_2O + 2H_2O\ (\text{gas}) \tag{3}$$

The temperature at which the evolved liquid water boils is, of course, virtually unaffected by changes in sample parameters. Some examples of the curves obtained using a constant sample mass of 80 mg and a heating rate of 10°C min^{-1} are shown in Fig. 1. With the largest particles (−14 +18 BS mesh) the first stage of decomposition occurs comparatively slowly, due to the small surface/mass ratio and the time taken for the evolved water to diffuse to the particle surface. The corresponding endothermic peak then tends to merge with that due to boiling of the evolved water (Fig. 1A). This is followed by a separate endothermic peak due to step (3).

Samples having a rather smaller mean particle size (−52 +72 BS mesh) showed three distinct and separate endothermic peaks (Fig. 1B). Step (1) now occurs more rapidly and is virtually complete by the temperature at which the endotherm due to boiling water becomes apparent. The peak temperature corresponding to step (3) is also slightly reduced.

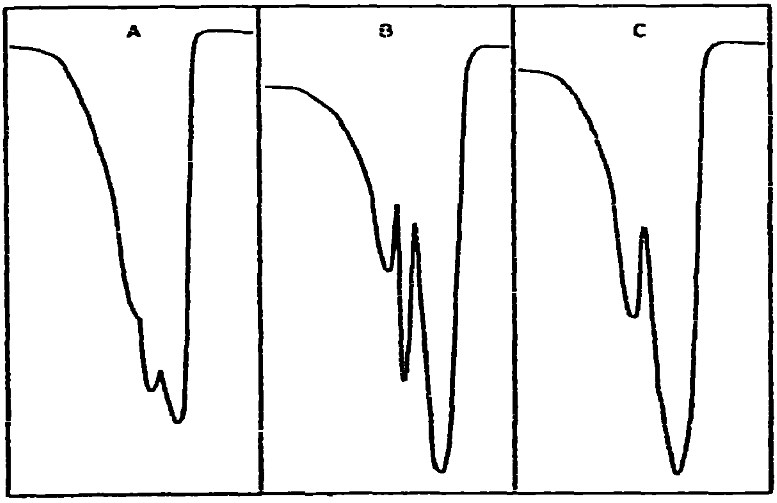


Fig. 1. DTA curves for $CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot H_2O$ in static air, using 80 mg samples heated at 10°C min^{-1}. (A) −14 + 18; (B) −52 + 72; and (C) −72 + 100 BS sieve fraction.

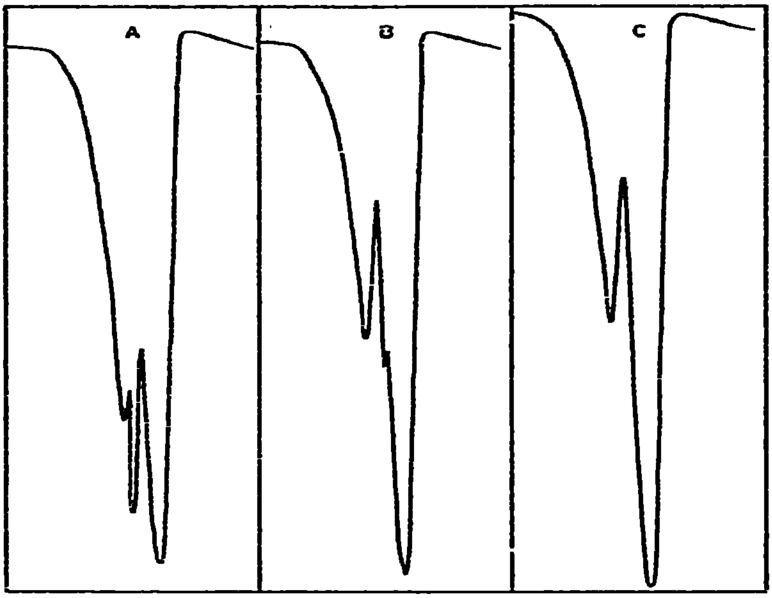
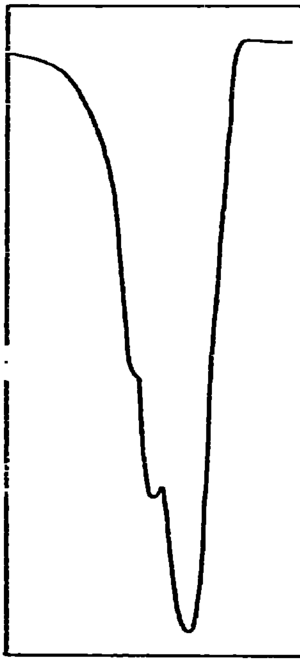


Fig. 2. DTA curves for $CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot H_2O$ in static air, using 80 mg samples heated at 5°C min^{-1}. (A) — 14 ÷ 18; (B) — 36 ÷ 52; and (C) — 52 ÷ 72 BS sieve fraction.



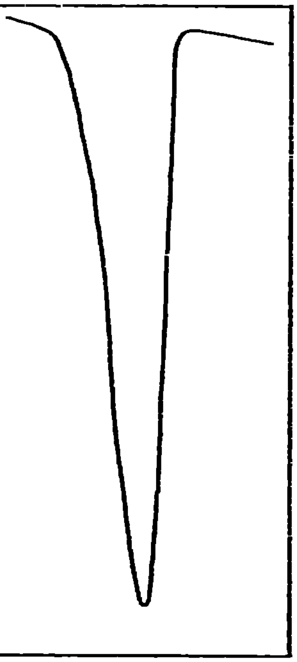


Fig. 3. DTA curve for $CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot H_2O$ in static air, using a 140 mg sample heated at 10°C min^{-1}. — 52 ÷ 72 BS sieve fraction.

Fig. 4. DTA curve for $CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot H_2O$ in static air, using an 80 mg sample containing 50 weight % alumina reference material, heated at 10°C min^{-1}. — 52 ÷ 72 BS sieve fraction.

Using even smaller particles (−72 +100 BS mesh), only two endotherms could be detected (Fig. 1C). Step (1) now occurs at a lower temperature still, as also does step (3). This results in the boiling endotherm (2) becoming completely obscured by that due to step (3), giving the appearance of a two-stage process.

When using samples with a wide particle-size distribution, under the same experimental conditions, three distinct peaks were always observed. Reducing the heating rate tends to cause the effects illustrated in Fig. 1 to become apparent for larger particle sizes. Hence, for a heating rate of 5°C min^{-1} and a sample mass of 80 mg, three separate endothermic peaks are now obtained with −14 ÷18 BS mesh particles (Fig. 2A). With −36 ÷52 BS mesh particles, the endotherm due to boiling has almost become obscured by that resulting from step (3), while it has disappeared altogether for particles in the −52 ÷ 72 BS sieve range (Figs. 2B, 2C).

If a large sample mass is used, diffusion of evolved water to the surface of the sample is impeded, resulting in much poorer resolution of the three endothermic processes. Using 140-mg samples and a heating rate of 10°C min^{-1}, three separate peaks could not be obtained, regardless of particle-size distribution. Optimum resolution was observed for the sample containing particles within the −25 ÷36 BS size range (Fig. 3).

The effect of sample dilution is perhaps more striking (and misleading) than the other variables investigated. Figure 4 shows a DTA curve for −52 ÷72 BS mesh $CuSO_4 \cdot 5H_2O$, heated at 10°C min^{-1}, using an 80-mg sample containing 50 wt.-% alumina as diluent. The three endothermic steps involved in the thermal decomposition now give rise to only one endothermic peak on the DTA curve.

The foregoing results thus clearly demonstrate the importance of standardising the sample parameters during DTA. In particular, it is necessary to consider the particle-size range and distribution, before comparing one DTA curve with another.

REFERENCES

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